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CONDUCTIVITY OF A QUARTER FILLED
NARROW BAND HUBBARD CHAIN

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ABSTRACT

The density of states and the conductivity is calculated for a quarter filled Hubbard chain with an interaction U_1 between nearest neighbours in the extreme narrow band and $U_0 \rightarrow \infty$ limit with and without polaronic effects. A comparison is made with experimental results on $\text{Qn}(\text{TCNQ})_2$ and the limitations of the model are shortly discussed.

АННОТАЦИЯ

Проводится расчет плотности состояний и проводимости для цепи Хаббарда, заполненной на четверть, на основе взаимодействия U_1 между близкими, в экстремно узкой полосе и в пределе $U_0 \rightarrow \infty$, с полярным взаимодействием и без него. Результаты сравниваются с экспериментальными данными относительно $\text{Qn}(\text{TCNQ})_2$. Обсуждаются недостатки расчетной модели.

KIVONAT

Az állapotsűrűséget és a vezetőképességet számítjuk ki egy negyedig betöltött Hubbard-láncrea U_1 kölcsönhatással a legközelebbi szomszédok között az extrém keskeny sávban és $U_0 \rightarrow \infty$ limitben, polaron kölcsönhatással és anélkül. Összehasonlítjuk a $\text{Qn}(\text{TCNQ})_2$ kísérleti adataival és röviden diszkutáljuk a modell korlátait.

One class of the highly conducting salts¹ of tetracyanoquinodimethan (TCNQ), of which the quinolinium salt $\text{Qn}(\text{TCNQ})_2$ is a typical example shows a broad maximum in the conductivity σ , below the maximum $\sigma(T)$ has an exponential behaviour¹, and above it is proportional to the inverse temperature². Various explanations have been suggested to account for this behaviour^{3,4}, it is however believed that Coulomb correlation effects play a significant role. The observation, that simple (1:1) salts have much lower conductivity than the complex (1:2) salts⁵ suggests that the on - site Coulomb interaction U_0 is much larger than the bandwidth D , in accordance with recent calculations giving $U_0 \sim 5$ eV, $D \sim 1$ eV⁶. The high conductivity (of around $100 \Omega^{-1} \text{cm}^{-1}$) of the complex salts rules out the possibility of phonon assisted hopping between states localized by random disorder, and then the low temperature insulating state is stabilized by long range Coulomb forces. In the 1:2 salts the conduction band is quarter filled in case of full charge transfer, and nearest neighbour interactions are sufficient to arrive at a band gap, and insulating ground state.

It has also been suggested^{7,8,9}, that interactions between the conduction electrons on the TCNQ chain and the neighbouring donors have a drastic effect due to coupling between the electrons and local vibrations and

polarization respectively.

In order to consider these effects we introduce the Coulomb interaction U_1 between electrons on the neighbouring TCNQ molecules

$$H_1 = U_1 \sum_{i\sigma\sigma'} n_{i\sigma} n_{i+1\sigma'} \quad / 1/$$

into the usual Hubbard Hamiltonian

$$H_0 = t \sum_{i\sigma} n_{i\sigma} + b \sum_{i\sigma} (c_{i\sigma}^\dagger c_{i+1\sigma} + c_{i+1\sigma}^\dagger c_{i\sigma}) + U_0 \sum_i n_{i\uparrow} n_{i\downarrow} \quad / 2/$$

where $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$, $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) creates (destroys) an electron on the i th site with spin σ , and $b = D/4$ is the tight binding transfer integral, together with the local polaronic and excitonic interaction which in both cases can be represented by¹⁰

$$H_p = g \sum_{i\sigma} Q_i n_{i\sigma} + \frac{1}{2} \Omega \sum_i (P_i^2 + Q_i^2) \quad / 3/$$

where g is the coupling constant, Q_i and P_i the coordinate and momentum of the local mode.

We calculate the density of states and the conductivity in the $U_0 \rightarrow \infty$ and $U_1/b \gg 1$ limit along lines first used by Bari⁹ for the half filled Hubbard case. We also make a comparison the calculated $\sigma(T)$ with experiment, however point also out the features which are not explained by the present model.

We first consider the effect of nearest neighbour

interactions only and discuss the influence of polaronic effects later. The Hamiltonian

$$H = H_0 + H_1 \quad / 4/$$

can be transformed in case of $U_0 \rightarrow \infty$ to a spinless Fermion system¹¹

$$H = t \sum_i n_i + b \sum_i (a_i^\dagger a_{i+1} + a_{i+1}^\dagger a_i) + U_1 \sum_i n_i n_{i+1} \quad / 5/$$

where a_i^\dagger (a_i) creates (destroys) an electron on the i th site but without spin and $n_i = a_i^\dagger a_i$.

The partition function in the $U_1/b \gg 1$ limit can be obtained in a straightforward way using the transfer matrix method

$$Z = \text{Tr} e^{-\beta(H - \mu N)} = \text{Tr} P^{N_s} = \lambda_+^{N_s} \quad / 6/$$

here N_s is the number of TCNQ molecules (number of sites)

μ is the chemical potential and for the quarter filled band $\mu = t + U_1$, P is the transfer matrix, it's largest eigenvalue is $\lambda_+ = 1 + \exp(\beta \cdot U_1/2)$.

The spectral function which is proportional with the electron density of states is given by

$$A_{ij}(\omega) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle \{a_i(\tau); a_j^\dagger(0)\} \rangle \quad / 7/$$

where the operators evolve in time τ according to

$a_i(\tau) = e^{iH\tau} a_i e^{-iH\tau}$. Performing the anticommutator we get

$$\{a_i(\tau); a_j^\dagger(0)\} = \delta_{ij} e^{-i[t + U_1(n_{i+1} + n_{i-1})]\tau} \quad / 8/$$

The thermal average in Eq/ 7/ is written in the following form

$$\langle \{a_i(\tau); a_j^\dagger(0)\} \rangle = \frac{\delta_{ij} e^{-it\tau}}{\sum} \text{Tr } P^{N-2} \cdot \tilde{P} \cdot \tilde{P}^* \quad / 9/$$

where P is the same transfer matrix as above except of elements corresponding to $i-1, i$ and $i, i+1$ sites are modified by the factor given by / 8/. The modified two terms are described by \tilde{P} and \tilde{P}^* respectively, \tilde{P}^* is the transposed matrix of \tilde{P} . Eq/ 9/ can easily be evaluated and measuring the energy from the Fermi level the spectral function is given by

$$A_{ij}(\omega) = \frac{1 + e^{\beta U_1}}{(1 + e^{\frac{1}{2}\beta U_1})^2} \left[\delta(\omega - U_1) + \delta(\omega + U_1) + \frac{4 e^{\frac{1}{2}\beta U_1}}{1 + e^{\beta U_1}} \delta(\omega) \right] / 10/$$

At $T = 0$ $A_{ij}(\omega)$ has two peaks separated by $2U_1$, with increasing temperature a central peak appears with increasing amplitude. The spectral function measures the probability amplitude of adding or removing an electron at a resultant energy change of ω to the system in thermal equilibrium. The origin of these peaks can be traced easily owing the equivalence of the Hamiltonian / 5/ with an anisotropic Heisenberg model with antiferromagnetic coupling¹². We have the following processes for one site excitations: (i) addition of an electron to an empty site which has two occupied neighbour sites; (ii) removal of an electron from an occupied site having two empty neighbour sites; (iii) addition (removal) of an electron to (from) a site which has one occupied and one empty neighbour sites. The $U_1/b \gg 1$ limit corresponds to the strongly anisotropic Heisenberg chain which has

at $T=0$ long range magnetic order. Consequently in our case empty and occupied sites are alternating periodically at $T=0$, and only excitations of type (i) and type (ii) exist resulting in two peaks in the density of states separated by $2U_1$. With increasing temperature the long range order breaks down progressively the process of type (iii) becomes effective leading to the appearance of the central peak.

Following Bari⁹ we derive $\sigma(\omega)$ by using the formula

$$\sigma(\omega) = \frac{\tanh(\frac{1}{2}\beta\omega)}{2L\omega} \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle \{F(\tau); F(0)\} \rangle \quad /11/$$

where

$$F = ieba \sum_i (a_i^+ a_{i-1} - a_i^+ a_{i+1}) \quad /12/$$

a is the lattice constant and L is the volume of the conducting TCNQ chain. The thermal average can be evaluated on the same way as before and

$$\sigma(\omega) = \frac{e^2 b^2 a^2 \tanh(\frac{1}{2}\beta\omega)}{2L\omega(1+e^{\frac{1}{2}\beta U_1})^3} \left[4e^{\beta U_1} \delta(\omega) + (e^{\frac{1}{2}\beta U_1} + e^{\frac{3}{2}\beta U_1}) (\delta(\omega+U_1) + \delta(\omega-U_1)) \right] /13/$$

and the dc conductivity is given by

$$\sigma(T) = \frac{e^2 b^2 a^2}{4L} \beta \frac{4e^{\beta U_1}}{(1+e^{\frac{1}{2}\beta U_1})^3} \quad /14/$$

When the polaron interaction / 3/ is included the electron and polaron part can be decoupled using the canonical transformation^{9,10}

$$h = e^{i\sigma\hat{S}} H e^{-i\sigma\hat{S}}; \quad \hat{S} = \sum_i p_i n_i; \quad \sigma = -g/\Omega \quad /15/$$

and the thermodynamic averages decouple to an electron and

a polaron parts. This leads to a shift of the corresponding energies $t \rightarrow t - g^2/\Omega$ and a broadening of the δ functions in the spectral function into Gaussian curves

$$\sqrt{\frac{2\pi}{\Gamma}} e^{-\frac{\omega^2}{2\Gamma}}$$

where

$$\Gamma = \frac{1}{2} g^2 \coth\left(\frac{1}{2}\beta\Omega\right)$$

as it can be seen in Fig. 1.

The conductivity can be evaluated similarly to the previous case giving

$$\sigma = \frac{e^2 b a^2 \tanh\left(\frac{1}{2}\beta\omega\right)}{L\omega(1+e^{\frac{1}{2}\beta U_1})^3} \sqrt{\frac{\pi}{\Gamma}} \left[4e^{\beta U_1} e^{-\frac{\omega^2}{2\Gamma}} + \left(e^{\frac{1}{2}\beta U_1} + e^{\frac{3}{2}\beta U_1}\right) \left(e^{-\frac{(\omega-U_1)^2}{2\Gamma}} + e^{-\frac{(\omega+U_1)^2}{2\Gamma}}\right) \right] \quad /16/$$

and for the $\omega = 0$ case

$$\sigma = \frac{e^2 b a^2}{2L} \beta \sqrt{\frac{\pi}{\Gamma}} \frac{1}{(1+e^{\frac{1}{2}\beta U_1})^3} \left[4e^{\beta U_1} + \left(e^{\frac{1}{2}\beta U_1} + e^{\frac{3}{2}\beta U_1}\right) 2e^{-\frac{U_1^2}{2\Gamma}} \right] \quad /17/$$

The temperature dependence of the conductivity is shown in Fig. 2. without and with polaron effects, the spurious low temperature upturn is similar to that found for the half filled case and discussed by Bari⁹. In order to demonstrate that the calculated conductivity faithfully represents the experimental situation in Fig. 3. we show a computer fit of Eq/17/ to the experimental data² on Qn(TCNQ)₂. The agreement is surprisingly good both below and above the maximum and leads to $U_1 = 0.088$ eV; $b = 0.009$ eV; $\Omega = 0.017$ eV; and $g = 0.018$ eV.

We hasten to add that we do not regard this good agreement as evidence that the conductivity is

exclusively determined by effects discussed above, as any model with a band gap of order kT_{max} should give a similar overall behaviour. We also note, that the parameters obtained by the fitting procedure are somewhat smaller than those obtained by first principle calculations. The latter calculations however usually result in characteristic energies too large comparing with experimental observation.¹³

Finally we mention that our model does not lead to a correct ground state which should be obtained only if more distant interactions between the electrons are considered too (therefore we do not expect good agreement with the measured conductivity at very low temperatures). The susceptibility is Curie - type in our model in contrast to the singlet ground state observed¹⁴. It is also evident that disorder effects play a crucial role in the TCNQ salts, thus the dc and ac conductivity are widely different below the maximum^{1,15}, in contrast to the calculated weak ω dependence (see Eq/16/).

This together with our previous conclusion suggests that both electron - electron and electron - polaron interactions (determining the band gap and the band widths) and disorder (leading to band tailing etc.) should be considered in an attempt to fully understand these types of materials.

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REFERENCES

1. SHCHEGOLEV I.F. Phys. Status Solidi 12, 9 (1972).
2. MIHÁLY G., RITVAY - EMANDITY K. and GRÜNER G. to be published.
3. COLEMAN L.B., COHEN J.A., GARITO A.F. and HEEGER A.J. Phys. Rev. B7, 2122 (1973).
4. BLOCH A.N., WEISMAN R.B. and VARMA C.M. Phys. Rev. Lett. 28, 753.
5. SIEMONS W.J., BIERTEDT P.E. and KEPLER R.G. J. Chem. Phys. 39, 3523 (1971).
6. SUHAI S. to be published. These parameters obtained by first principal calculations.
7. CHAIKIN P.M., GARITO A.F., and HEEGER A.J. J. Chem. Phys. 58, 2336 (1973).
8. BENI G. PINCUS P. and KANAMORI J. Phys. Rev. B10, 1896 (1974).
9. BARI R.A. Phys. Rev. B9 4329 (1974).
10. HOLSTEIN T. Annals of Phys. 8, 329 (1961) and 8, 343 (1961).
11. OVCHINNIKOV A.A. Zh. Eksp. Teor. Fiz. 64, 342 (1972) [Sov. Phys.-JETP. 37, 176 (1973)].
12. The two model are connected by the so called Jordan - Wigner transformation. BULAEVSKII L.N. Sov. Phys., -JETP. 16, 685 (1963).
13. EPSTEIN A.J., ETEMAD S., GARITO A.F. and HEEGER A.J. Solid State Commun. 9, 1803 (1971).
14. MILJAK M., JÁNOSSY A. and GRÜNER G. to be published.
15. HOLCZER K., MIHÁLY G., JÁNOSSY A. and GRÜNER G. to be published at the IVth International Symposium on the Organic Solid State 1975 Bordeaux.

CAPTIONS

Fig. 1. Spectral function in quarter filled Hubbard chain with polaron effects at $T = 0$ and at $T = 200^\circ\text{K}$.
($g = \Omega = 200^\circ\text{K}$.)

Fig. 2. Temperature dependence of the conductivity. Full line: without polaron effects, dotted line with polaron effects ($g = \Omega = U_1/3$).

Fig. 3. Calculated and measured conductivity for Qn(TCNQ)_2 .

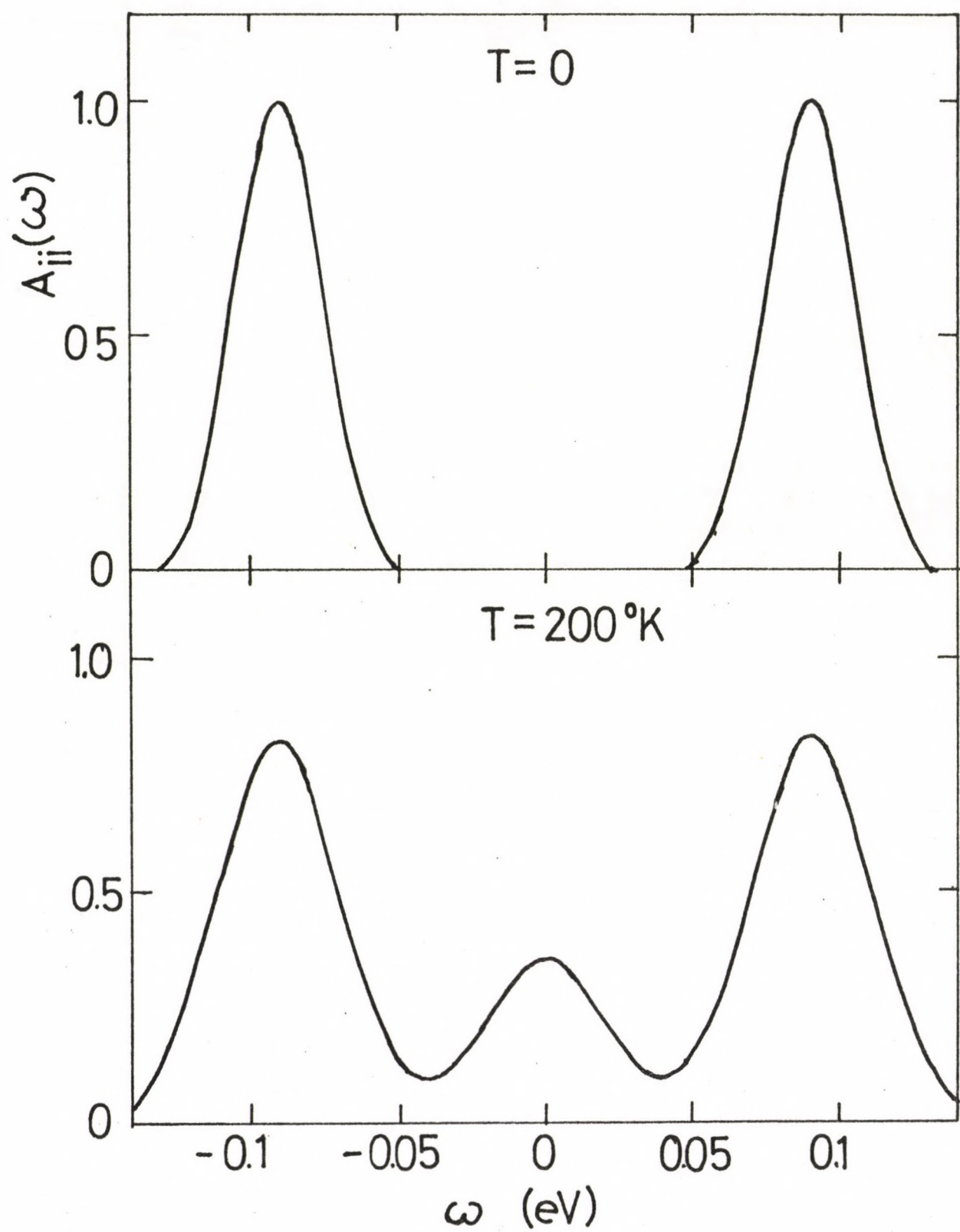


Fig. 1.

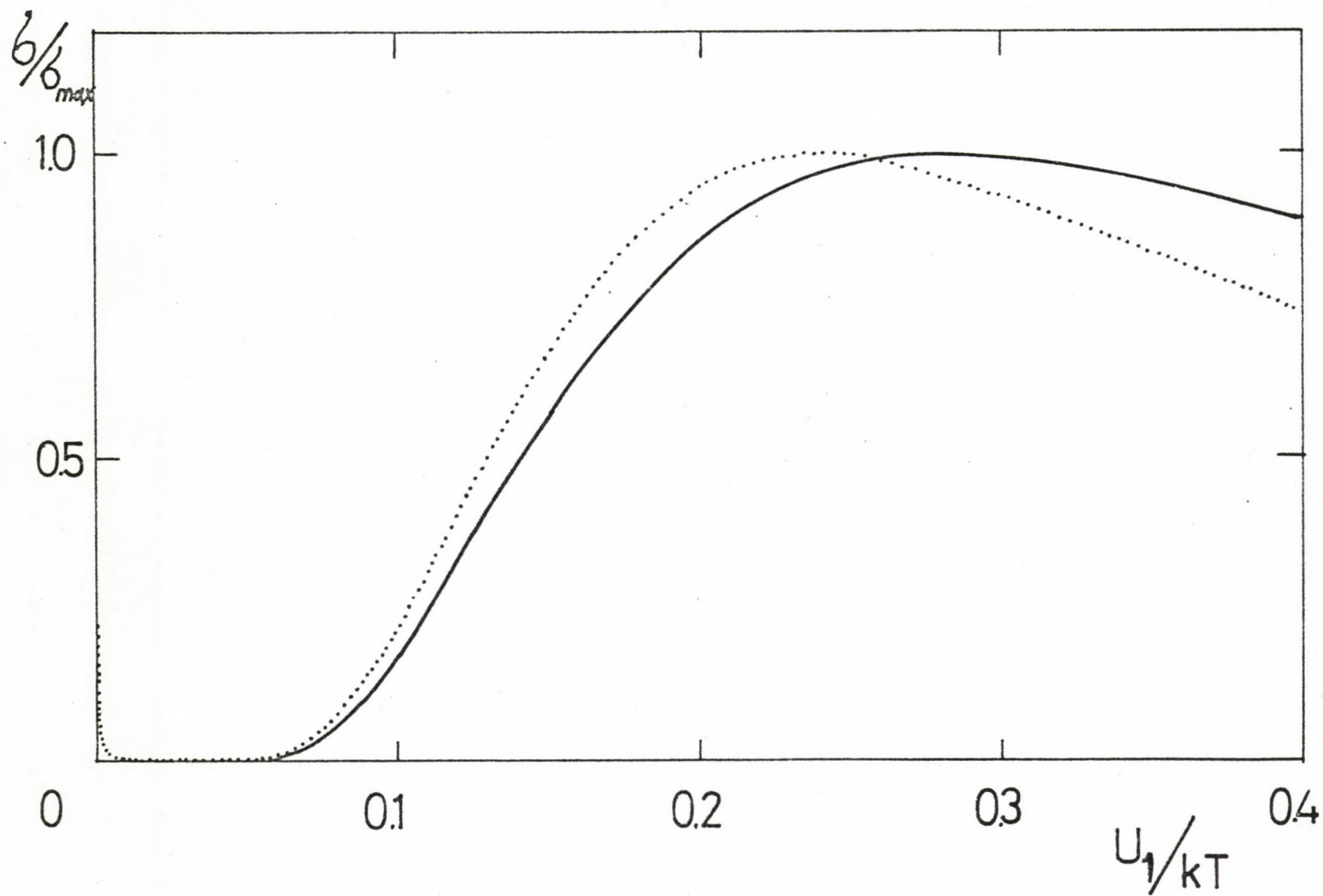


Fig. 2

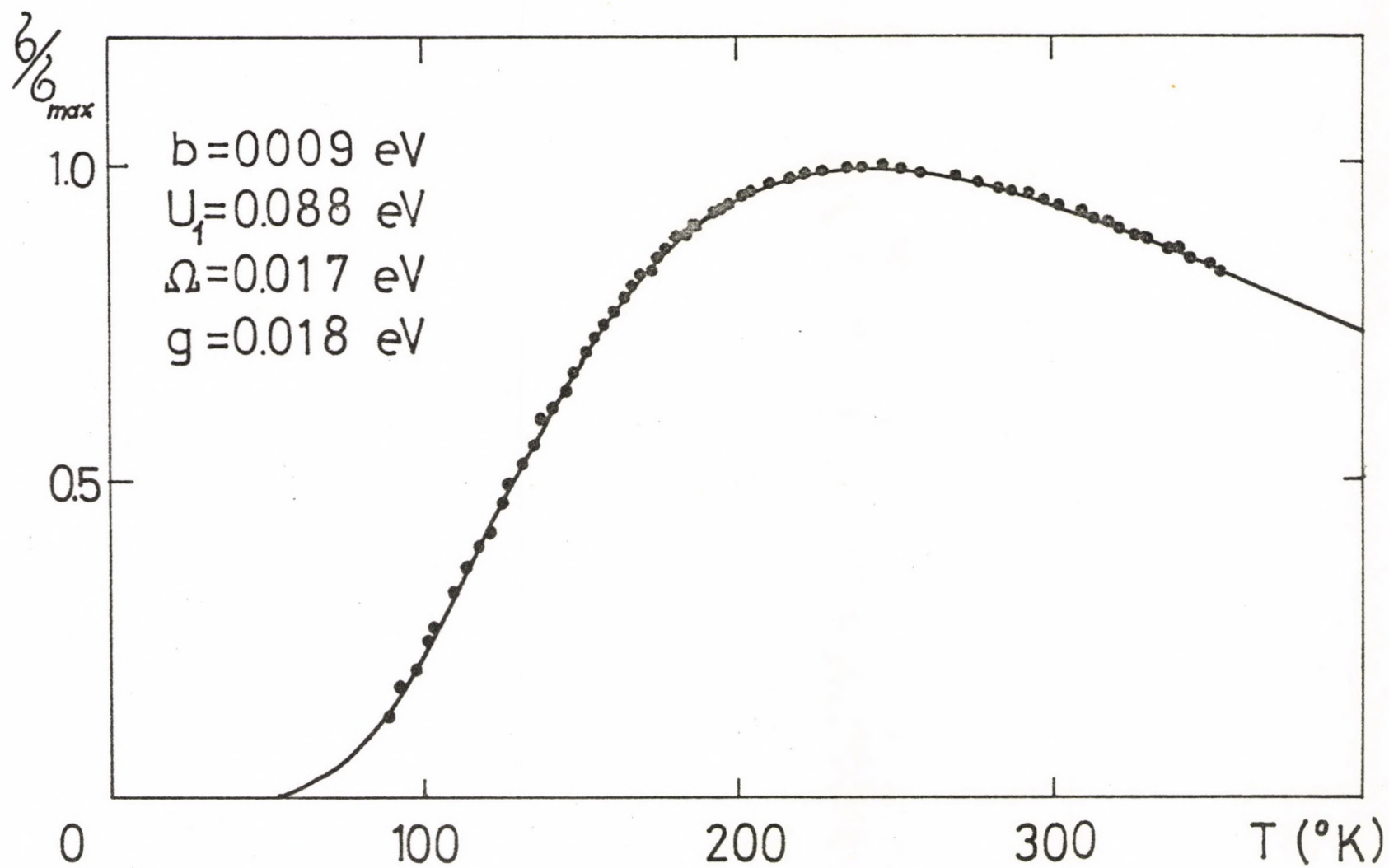


Fig. 3



Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Kósa Somogyi István, a KFKI
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